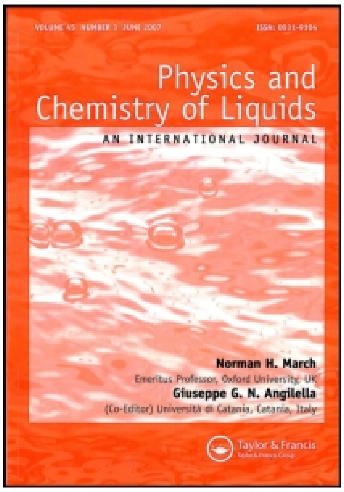

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Viscosity of Molten NaCl, $NaBF_4$ and KBF_4

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The viscosities of molten $NaBF_4$ and KBF_4 were determined over a 120°C interval and the viscosity of molten NaCl was redetermined over a 200°C interval by use of an oscillating cup viscometer. The viscosities of all three samples followed an Arrhenius type temperature dependence. The measured viscosity for NaCl agreed better with predicted values and the trend established by the other sodium and potassium halides than did previous determinations. The Batchinskii free volume concept of viscosity held for the sodium and potassium halides and the two MBF_4 salts. An equation based upon a hard-sphere model predicted viscosity values in agreement with experimental values for the alkali metal halides and KBF_4 but was not suitable for $NaBF_4$.

INTRODUCTION

This study reports the first viscosity measurements of the molten salts $NaBF_4$ and KBF_4. The BF_4^- ion possesses tetrahedral symmetry in the sodium salt.[1]

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[‡] Operated for the USAEC under Contract No. W-7405-ENG-26.

Raman spectral measurements[2] indicate that the tetrahedral symmetry is retained in $NaBF_4$ melts and that there is no evidence to suggest ordering in the molten state as implied for molten nitrates.[2] To a first approximation, therefore, the molten BF_4^- ion may be considered spherical with a radius of 2.11 Å, intermediate to the Br^- and I^- ions. Experimentally, the volumetric properties[3] of molten $NaBF_4$ and KBF_4 have been shown to be similar in behavior to their respective alkali metal iodides. For these reasons, the viscosities of the MBF_4 melts are compared with those of the alkali metal halides.

The viscosity of molten NaCl was remeasured because of conflicting literature data.[4,5] The use of these literature data indicated that the viscosity of NaCl at its melting point and its activation energy for viscous flow were anomalous when compared with the trend set by the other sodium and potassium chloride, bromide and iodide melts (see Table 3).

EXPERIMENTAL

Apparatus and materials

The viscosities of the molten salts were measured with a semi-automated version of the torsional oscillating cup viscometer.[6] In this instrument the fluid was contained in a sealed cylindrical cup. The cup, suspended by a torsion fiber, is part of an oscillating pendulum, contained in a vacuum chamber (5×10^{-6} to 1×10^{-4} torr). The viscosity of the fluid was determined from the damping effect of the fluid in the cup upon the oscillating pendulum, as previously described.[7]

In the present investigation an electromagnetic system was used to measure the oscillations of the pendulum. A wound copper coil attached to the pendulum was positioned in the hollow core of a permanent magnet. As the pendulum and coil oscillated within the uniform magnetic field, an emf was produced. The emf, in the form of a damped sine wave, was 90 degrees out of phase with the amplitude of the oscillating pendulum but directly proportional to it. The emf was recorded with both an oscillographic recorder and a digital integrator. The digital integrator determined the area between the traced damped sine wave and the base line. Area measurements were used to calculate the damping constant since the area determinations were found to be more precise than the amplitude measurements.

Logarithms of the observed readings of the area were plotted against the number of oscillations. These values were fitted by the least squares method to a straight line so that the slope, called the logarithmic decrement, was determined. The period of oscillation was obtained from the oscillographic recording chart and a knowledge of the chart speed. The temperature of each viscosity determination was measured with a chromel-alumel thermocouple positioned near the cup but not touching it.

Chemicals

The NaCl samples used in the viscosity determinations were taken from Baker and Adamson reagent grade material. The recrystallized $NaBF_4$ and KBF_4 samples were prepared as previously described.[3]

Procedure

Two samples of NaCl were dried at 250°C overnight and loaded into the viscometer capsules. Two samples each of $NaBF_4$ and KBF_4 were prepared and loaded into capsules. Weights of the salts and their capsule sizes are listed in Table 1. Capsules containing the salts were evacuated at $\sim 30 \times 10^{-3}$ torr for 20 hours in the glovebox where capsules were welded shut. The gloveboxes were purged twice with purified helium and the weld accomplished with an argon-arc torch. During the welding, the capsules were kept in a copper block to rapidly remove the heat generated by the welding, thus preventing possible decomposition of the MBF_4 samples. Confirmation of successful heat dissipation was obtained from an absence of weight changes of the capsules during the welding.

The reported viscosities represent the average of three logarithmic decrement determinations at each temperature. In general, the logarithmic decrements, reproducible to ± 1%, yielded viscosity with a precision measurement of ± 2%. Reproducibility between two different samples of each salt was approximately ± 5% for $NaBF_4$ and somewhat better for KBF_4. This appreciable uncertainty, particularly for $NaBF_4$, may be related to the difficulty described by Barton, *et al.*[8] in obtaining stoichiometric material. There is another problem associated

TABLE 1

Dimensions and contents of capsules

Capsule no.	Sample	Weight of contents, g	Internal diameter, cm	Moment of inertia for system g-cm^2
Na-9	$NaBF_4$	26.6985	1.742	141.47
Na-10		28.1823	1.748	,,
K-6	KBF_4	21.2064	1.744	,,
K-7		24.1104	1.746	,,
1	NaCl	14.3510	1.481	139.74
2		14.9844	1.481	394.92

with the tetrafluoborate which should be noted, namely the dissociation in the liquid to MF and BF_3. Its effect on the experimental results is, however, well within the precision of the measurements given above because the experiments were performed in sealed containers with very small free volume so that the amount of dissociation was probably less than 0.1 mole %.

RESULTS

The viscosity data for NaCl, $NaBF_4$ and KBF_4, Table 2 and Figures 1 and 2, were obtained from two samples for each salt, noted in Table 1. For a more accurate establishment of the viscosity of NaCl, widely different experimental parameters were used when both the moment of inertia and the torsion fiber were changed for each capsule. For Capsule No. 1, which had the largest logarithmic decrement, the precision of an individual data point was approximately ±0.01 cP while it increased to ±0.04 cP for Capsule No. 2 for which the logarithmic decrement was only one-half as large. A least-squares fit of the data was used to obtain the coefficients of the linear equation,

$$\ln \eta = -7.3522 + 6260/RT.$$

The inclusion of all the data from both determinations resulted in a standard deviation of ±0.06 cP.

The activation energy and viscosity of NaCl at the melting point are 6.26 kcal $mole^{-1}$ and 1.21 cP, respectively. It can be seen from Table 3 that, unlike the results of the earlier data[4,5] these new parameters establish a trend in the sodium halides similar to what is observed in potassium halides. For this reason we feel the present viscosity is probably more accurate than the earlier measurements.

The viscosity data for $NaBF_4$ and KBF_4 also follow Arrhenius-type equations (Figure 2). The coefficients obtained from a least-squares fit of the data are

$$NaBF_4\colon\ \ln \eta = -7.1476 + 4780/RT \text{ and}$$
$$KBF_4\colon\ \ln \eta = -6.9629 + 4530/RT$$

and yield activation energy of 4.78 and 4.53 kcal $mole^{-1}$, respectively. Like the corresponding alkali metal halides with a common anion (see Table 3) the activation energies of the sodium and potassium tetrafluoroborate are nearly the same. Furthermore, the activation energies parallel the lower melting points and heats of fusion when compared to the alkali metal halides.

On the assumption that the ions are spherical and that their size is important in determining the viscosity, one would expect the behavior of the BF_4^- ion to be similar to that of the alkali metal bromides or iodides. A comparison of the viscosities of the BF_4^-, salts with the corresponding iodides at their melting

TABLE 2

Measured viscosity of NaCl, $NaBF_4$ and KBF_4

Temp. °C	Density g/cm^3	Period sec.	Log. dec. X10^2	Viscosity cP
NaCl Capsule No. 1				
833	1.54	2.848	1.643	1.08
875	1.52	2.848	1.618	1.02
927	1.49	2.848	1.522	0.86
929	1.49	2.848	1.508	0.84
958	1.47	2.848	1.511	0.85
977	1.46	2.848	1.527	0.85
1025	1.43	2.848	1.435	0.72
NaCl Capsule No. 2				
872	1.52	5.730	0.774	1.01
914	1.50	5.732	0.765	0.96
956	1.47	5.732	0.773	0.97
999	1.45	5.732	0.672	0.66
$NaBF_4$ Capsule No. 9				
426	1.94	2.013	4.019	2.42
434	1.94	2.016	4.059	2.47
448	1.93	2.014	3.896	2.22
471	1.91	2.011	3.826	2.11
509	1.88	2.009	3.515	1.69
$NaBF_4$ Capsule No. 10				
432	1.94	2.040	4.163	2.26
453	1.92	2.038	4.119	2.18
477	1.91	2.038	3.941	1.94
513	1.88	2.033	3.655	1.60
KBF_4 Capsule No. 6				
602	1.72	2.046	2.620	1.28
641	1.69	2.038	2.566	1.20
681	1.66	2.040	2.423	1.03
KBF_4 Capsule No. 7				
585	1.73	2.057	3.051	1.37
623	1.70	2.053	2.884	1.18
625	1.70	2.053	2.861	1.16

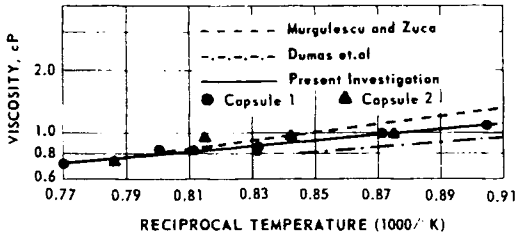

FIGURE 1 Comparison of the present investigation of the viscosity of NaCl as a function of reciprocal temperature with two previous investigations.[4,5]

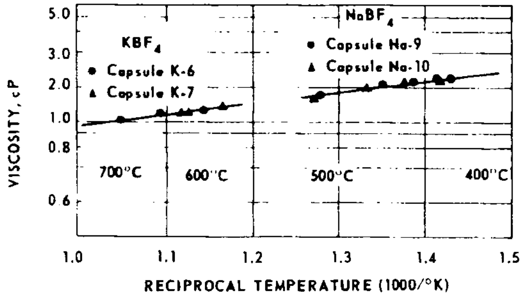

FIGURE 2 Measured viscosities of $NaBF_4$ and KBF_4 as a function of reciprocal temperatures.

points, as given in Table 3, shows good agreement in the case of the potassium, but not for the sodium salts.

DISCUSSION

The viscous behavior of these melts are compared with several presently held correlations and models describing viscous flow in liquids. In regard to the temperature dependence of viscosity, Davies and Matheson[9] have noted that spherical molecules or ions exhibit viscosity equations which follow Arrhenius type temperature dependence, while liquids containing non-spherical molecules or ions deviate from Arrhenius behavior. Because the viscosity data for NaCl, $NaBF_4$ and KBF_4 (Figures 1 and 2) follow Arrhenius behavior, at least within the experimental error, the assumption can be made that the ions are nearly spherical.

A correlation which has recently received renewed attention[10] is the "free-volume" concept of viscous flow originally proposed by Batchinskii[11] in 1913.

TABLE 3

Viscosity at the melting point and activation energy

Salt	T °K	ΔH_f^a kcal mole^{-1}	Visc. at T_m cP	E_v kcal mole^{-1}
NaBF$_4$	680	3.25	2.69	4.78
NaI	935	5.64	1.52	5.67
NaBr	1023	6.24	1.46	5.13
NaCl	1073	6.69	1.21	6.26
			1.49	8.69[b]
			1.01	4.95[c]
KBF$_4$	843	4.30	1.41	4.53
KI	958	5.74	1.55	5.34
KBr	1008	6.10	1.26	5.16
KCl	1043	6.27	1.23	6.52
			1.05	5.52[c]

[a] A. S. Dworkin and M. A. Bredig, *J. Phys. Chem.*, 64, 269 (1960) and Ref. 22

[b] Ref. 4

[c] Ref. 5

This simple equation is

$$\eta = \frac{B}{V_\ell - c} \qquad (1)$$

where η = viscosity

V_ℓ = molar volume of liquid, and B and c are constants.

Murgulescu[12] has applied this correlation to many molten slats and has shown that for highly ionized univalent-univalent salts, the term "c" is identified as the molar volume of the solid at the melting temperature, V_s. For molten salts in which association occurs, the value of "c" is much less than the volume of the solid at the melting point. Copeland and Christie[13] have shown that this simple equation describes the behavior of molten alkali metal nitrates over a range of temperatures and pressures.

Plots of the data were made with the Batchinskii equation rearranged in the form

$$\frac{1}{\eta} = \left(\frac{1}{\rho}\right)\left(\frac{M}{B}\right) - \frac{c}{B}$$

where ρ = liq. density and M = molecular weight. Straight lines were obtained for the data when fluidity ($1/\eta$) were plotted against the reciprocal of density ($1/\rho$) and values of B and c were determined. The data for NaCl, $NaBF_4$ and KBF_4 are taken from the present measurements, and the data for the other alkali metal halide salts were taken from the compilation by Janz,[14] except as noted. The values of "c" determined for the alkali metal halides and the tetrafluoroborates show good correlation with V_s (Table 4).

Copeland and Christie noted that the success of the Batchinskii relationship for simple ionic melts supports the view expressed by Rice[15] that "hard-sphere-like forces tend to control transport behavior".[13] Based on this suggestion, a hard-sphere description of viscosity, applied with some success to noble gas and metallic liquids, was tested for these molten salts. This viscosity relationship is based upon the self-diffusion model for a dense fluid, derived by Ascarelli and Paskin,[16] who made the assumptions: (1) that the Enskog hard-sphere expression is valid for the self-diffusion of a molecule of finite size in a dense fluid, (2) that the packing density of all normal liquids is the same at the freezing temperature and (3) that the hard-sphere gas pressure is balanced by the cohesive energy density term in the virial expansion of the Van der Waal's equation. Vadovic and Colver[17] modified the original equation by using a different hard-sphere equation of state and a term to correct for backscatter.

The relationship between self-diffusion, D, and viscosity, η, in a hard-sphere fluid at densities comparable to a liquid near its freezing temperature has been recently determined by Alder, Gass and Wainwright[18] by use of computer simulated transport phenomena; this relationship, expressed in radii instead of diameters as originally given, is

$$\frac{D\eta\ell}{kT} = 0.084 \qquad (2)$$

where ℓ = hard sphere radius
k = Boltzman constant and
T = temperature

A combination of this latter relationship with the equation for D from Vadovic and Colver yields the viscosity relationship,

$$\eta = 0.23\,\frac{\mu}{\mu_m}\,\frac{1}{\ell^2 N}\;-\left[\frac{RTM}{\pi}\right]^{\frac{1}{2}}\left[9.385\,(T_m\rho/T\rho_m)-1\right] \qquad (3)$$

where μ = packing fraction
ρ = density
N = Avogadro's number

and the subscript "m" refers to the given property at the melting point.

TABLE 4

Comparison of molar volumes

Molten salt	T_m, °K	$V^{exp.\,a}_{liq.}$, cm^3	$V^{exp.\,a}_{S}$, cm^3	$V^{calc.\,b}_{S}$, cm^3
$NaBF_4$	680	56.09	50.70[c]	51.90
NaI	935	54.72	46.14	49.00
NaBr	1023	43.95	36.02	38.92
NaCl	1073	37.56	30.19	32.71
KBF_4	843	71.40	59.3[d]	61.48
KI	953	67.83	58.46	58.37
KBr	1008	55.95	48.05	50.05
KCl	1043	48.80	41.60	43.80

[a] From experimental density or x-ray data

[b] Calculated using the Batschinskii equation

[c] C. W. F. T. Pistorius, J. C. A. Boeyens and J. B. Clark, *High Temp. High Pressure, 1, 41,* (1969)

[d] Assuming 57.7 cm^3 at 300°C [C. Finback and O. Hassel, *Z. Phys. Chem.* (Leipzig) *32B,* 433 (1936)] and the general relationship:

$V_{843} = 57.7 \exp [1 \times 10^{-4} (843\text{-}573)]$

Although Equation 3 appears to contain two adjustable parameters, they are related, however, by the equation

$$\ell = [3\, M\mu/4\pi\, \rho N]^{1/3} \qquad (4)$$

Consequently, when either ℓ or μ are defined, a unique solution exists for Equation 3. Ashcroft and Lekner[19] have pointed out that the structural data for rare gas and liquid metals are satisfactorily correlated when $\mu = 0.45$ at the melting temperature. This same packing fraction is assumed for the molten salts. In addition, because these molten salts are composed of two particles, it is necessary to assume that the "average" weight of the moving particle is one-half of the molecular weight. When these assumptions are introduced into Eq. 4, "average" hard-sphere radii are obtained (see Table 5) which are approximately 4 to 9% greater than one-half the sum of the cation and anion crystalline radii of the molten salts. This observation probably reflects the large volumetric change upon melting displayed by the fused salts.

Based upon the derived values for ℓ, the viscosities of the alkali metal halide salts are calculated by Equation 3 (Table 5) and compared with the experimental

TABLE 5

Predicted viscosity at T_m

Molten salt	Radius, Å crys. [a]	HS [b]	Viscosity, cP Pred.	Exp.
NaCl	1.38	1.50	1.31	1.21
NaBr	1.45	1.58	1.52	1.46
NaI	1.56	1.70	1.51	1.52
$NaBF_4$	1.51	1.71	1.09	2.69
KCl	1.57	1.63	1.22	1.23
KBr	1.64	1.71	1.38	1.26
KI	1.75	1.82	1.39	1.55
KBF_4	1.70	1.85	1.11	1.41

[a] Crystallographic radius = $(r_{cation} + r_{anion})/2$

[b] Hard-sphere calc. by Eq. 4

values. For such a comparison, it should be noted that the various experimental values for the viscosity of NaCl at the freezing point differ by ±0.2 cP (see Figure 1). If such an experimental uncertainty exists for all the alkali metal halides listed, then the predicted values show remarkably good agreement with the experimental values. The comparison does indicate, however, that for KI the predicted value tends to be too small, and the effects of polarization should be considered if the accuracy of the experimental data justify it.

Although the BF_4^- ion is tetrahedral, the predicted viscosity of KBF_4 (Table 5) appears reasonable, only 10% lower correlation than between the experimental and predicted values for KI. Conversely, the predicted viscosity for $NaBF_4$ is much less than the experimental value. The success of the hard-sphere model for KBF_4 suggests that the poor correlation for $NaBF_4$ may be related to parameters used in Equation 3, such as the melting temperature.

The melting temperature of a substance reflects the difference in internal energy of the solid phase compared with that of the liquid phase. Several physical measurements of the high temperature phase of $NaBF_4$, such as its crystal structure,[20] its quadrupole coupling constant, and the extraordinarily short relaxation time of the fluorine atom in the anion,[21] indicate that the internal energy may be larger than normal with the result that the melting temperature and heat of fusion for this salt are abnormal when compared with potassium, rubidium and cesium tetrafluoroborates.[22] As a result, the solid-liquid correlations implied by use of the melting temperature in Equation 3 are not able to predict the viscosity values.

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